SCIENCE FOR CERAMIC PRODUCTION

Inorganic nonmetallic materials (ceramics, glasses, binding materials and composites based on them) are acquiring a wide application range and it is expected that in the XXIst century, the rate of their development will prevail over other kinds of material. All of the properties of a material are determined by its structure, understood as a scale ranging from a single atom to the part as a whole. The use of these materials in devices and structures is hampered by the problem of brittleness. The reproducibility of the structure in brittle materials, which determines the presence of stress concentrators, is of primary importance for stabilizing the mechanical properties.

The Russian Ceramic Society organizes a discussion on the problems of the reproducibility of the quality of inorganic nonmetallic materials in the aspect of solution to the problem "composition – structure – property".

Vice President of the Russian Ceramic Society
Member of the Russian Academy of Sciences
P. D. Sarkisov

The Editorial Board begins a discussion of problems of improving the quality of products made of ceramics and glasses within the framework of the information service of the Russian Ceramic Society. The topic of the discussion will be "Problems of reproducibility of the structure and properties (quality) of articles made of ceramic materials".

Under the conditions of the market economy, improvement of the quality of products is decisive for their competitiveness and the commercial success of the producers. In articles made of glass and ceramics, which belong to the class of brittle materials, the quality is especially closely connected with their structure. The Editorial Board hopes that a discussion devoted to ways of controlling the structure and, hence, the properties of ceramic and glass articles will be timely and useful.

Editorial Board of "Glass and Ceramics"

UDC 666.3:620.192

STABILITY OF THE QUALITY OF ARTICLES IN THE CERAMICS INDUSTRY

A. V. Belyakov[1] and V. S. Bakunov[1]

Translated from Steklo i Keramika, No. 2, pp. 14 – 18, February, 1998.

The prospects for improving the quality of articles from ceramics are considered from the standpoint of synergetics, i.e., the science studying the self-organization of systems. The main problem to be solved by production engineers consists in determining the bifurcation points, establishing methods for controlling the behavior of the system in them and, sometimes, eliminating the bifurcations. Sintering of binary oxides and their mixtures is considered as an example for showing that the methods of mathematical design of experiments make it possible to determine and eliminate bifurcation points and reduce the level of noises in them, which improves the quality of the articles.

As a rule, the quality of a part is understood as the degree of its correspondence to this or that purpose. But how should we approach the measurement of the quality of a ceramic as a material perceived by us from aesthetic, emotional and rational standpoints? Until recently, it was impossible to "check harmony by algebra." In passing along this way, we have not walked far from the "golden section" introduced by Leonardo da Vinci, although we have already started to write about the beauty of fractals [1] and can understand such expressions as "a nice process," "an expressive formula," or "a brilliant solution." It is especially difficult to speak about the quality of ceramic articles, which can be a subject of art and at the same time a special-purpose material with strictly defined properties.

We will consider here the quality of ceramic articles as a category of the reliability of attaining this or that property in

[1] D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia; "IVTAN", Moscow, Russia.

the manufacturing process. We will speak of objective characteristics that can be measured by existing devices. It should be noted that the concept of "good" or "poor" quality often includes our insufficient knowledge of the essence of phenomena that affect this or that parameter. Let us explain what we mean. A poor-quality "worm" superconductor does not exhibit superconductivity at the temperature of liquid nitrogen, a poor-quality structural ceramic has insufficient fracture toughness, poor-quality jewelry clouds with time, etc. At the same time, we do not yet know ways of attaining the requisite quality.

First of all, the concept of the high quality of an article in the actual case includes the aspect of the stability of the parameters of its properties in space and time and only then the level of these parameters. For example, building bricks can have more or less high strength in an actual batch, but the whole batch should be rejected (classified as a lower grade) if the strength values turn out to be scattered in tests.

We considered the concept of quality with respect to the stability of the properties exhibited by a ceramic during its production and in service. In [2], we presented the general approaches to the problem from the standpoint of the thermodynamics of nonequilibrium processes [3 – 5]. Proceeding from them, we can state that the causes of the variation of the properties of a ceramic lie not only in fluctuations of the composition and properties of the initial raw materials, insufficient knowledge of the processes and improper control over the conditions of the processes. In the general case, the instability of the properties is a consequence of the probabilistic nature of the fundamental laws that describe processes in the material world. Quite strong actions on the system as compared to the noise level (internal fluctuations and external perturbations) make the system change from a stable state to an unstable one, and then again to a stable state. In the unstable state (bifurcation), the evolution of the system obeys a probabilistic law, which is the reason behind the variations in its final state, the indeterminacy of the dissipative structures formed by the system in the process of self-organization in order to dissipate effectively the external actions. Such structures can consist of existing or newly formed structural components [6].

Based on the general positions considered in thermodynamics, we suggested general approaches to increasing the stability and reproducibility of the structure and properties of ceramics in the processes of their manufacturing and service [2]. The main task of the production engineer consists in making the evolution of the system predictable. Here we see two promising directions, namely, the creation of conditions for decreasing the degree of nonequilibrium of the processes in regions of the unsteady state of the system and purposeful creation of structures to be used by the system as dissipative ones under the actual conditions of an external load.

It should be noted that the determining role of the bifurcation points in the evolution of the system is obvious both in conducting processes for fabricating ceramics with the requisite quality and under the conditions of their service when the attained quality is released. We will try to concentrate on the main processes of the first case because examples of the second can be found in [7].

We will begin with some problems of mass transfer, which plays the determining role in ceramics technology and thus manifests itself in the majority of bifurcations that occur in the production of ceramics. The degree of nonequilibrium of the reaction of the system to an external action depends on the rate of intensification of the latter. The rate of internal self-organization, i.e., the creation of new dissipative systems or use of available ones, determines the relaxation rate; the higher the relaxation rate, the closer the evolution to quasiequilibrium conditions. Thus, the degree of nonequilibrium of the processes is determined by the difference in the rate of increase of the external action and the rate of its dissipation (i.e., relaxation).

In an actual production process, the main role is played by the processes of transfer of substance that are known to occur under the effect of a gradient of the thermodynamic potential. The latter is established in the presence of concentration, temperature, mechanical force or electric field gradients. The realization of gradients is connected with the motion of material particles, ions or their cooperation. In order to make the description more convenient, we can introduce virtual structural components (structural defects like vacancies, dislocations, boundaries, etc.) [2]. On one hand, we do not deviate here from physical reality and on the other hand we considerably simplify the laws that describe the occurrence of the processes.

Thus, when fabricating a ceramic and in the process of its service, we deal with the real components of dissipative structures or with their defects (i.e., virtual components) that possess a certain hierarchy (the case of a solid body was considered in [6]). The rate of the relaxation processes in such a system is determined by the physicochemical conditions and the inertness (i.e., mass) of the structural components at various levels of the hierarchy; on application of an external action, all of the relaxation processes occur in parallel and their weighted rate approaches that of the most rapid process. Therefore, in order to resist the action actively, the system first uses the available dissipative structures and then, at a low rate (or with a small action), can create new ones. The most rapid relaxation processes under a load consist in deformation of the elastic force field of chemical bonds followed by a shift in and motion of the structural elements with an increase in their mass. It should be taken into account that in a heterophase system (for example, solid body – liquid) the phenomena are complicated by the differences in the chemical bonds in each phase; as a rule, the determining role belongs to the processes in the liquid.

Based on the mentioned concepts, we can state that the main problem of the production engineer consists in determining the bifurcation points and the ways of controlling the behavior of the system at these points, and sometimes eliminating the bifurcations. This requires knowledge of the quantitative relations describing the occurrence of the process, i.e.,

the mathematical description of the evolution of the system and its properties. The numerical expression of the parameters of the properties is a rather simple operation, but the description of the structure is a nontrivial problem solved at present with fractal geometry [8, 9]. The notion of a fractal has not been defined exactly. As a rule, it is understood as a structure (a set of structures) which consists of parts similar to the whole in a certain sense (Mandelbrot [8]). There is evidence that the structure of an actual object can be described from the standpoint of topology by fractals that have long been known theoretically and are called geometric "monsters" [10]. These are multidimensional formations possessing a certain orderliness with respect to pure disorder, which is analogous to dissipative chaos. It is natural that attempts have been made to describe dissipative structures with fractals, where the invariance of the sets with respect to scale changes plays an important role. For example, the formation of particle aggregates (clusters) is described successfully by the evolution of fractals [11] described by mathematical laws.

It is important that an actual structure is usually described as a set of fractals rather than a single fractal. Such a set consists of interrelated fractal subsets, i.e., multifractals. In other words, a multifractal consists of a finite number of embedded self-similar fractal structures, i.e., an ensemble of interpenetrating sets or their multifractal spectrum. The multifractal measure of a structure characterizes topologically the distribution of the i-th fractal in the multifractal. With allowance for thermodynamic formalism, such a state can be represented as a statistical ensemble of a set of particles. Consequently, it is possible to describe the evolution of the structure of a real object quantitatively and place it into correspondence with the variation of the properties, which was proved in recent works devoted, for example, to aggregation processes, gel formation [11, 12], and diffusion in liquid and solid phases [13, 14].

Thus, the instability of the properties of a ceramic is determined by the presence of structural inhomogeneities, i.e., its multifractal nature. The set of parts in one batch and a set of batches can be described by analogy. The objective parameters that characterize the scattering of the properties determined by the structure are given by mathematical statistics. Without going into details of this science and its application in experiments [13 – 16], we will state that it makes it possible to establish the reliability of the results, the range of their variation, etc. However, in order to use this mathematical apparatus correctly, we must have a considerable number of objects in a batch and a lot of batches. As a rule, this procedure is carried out in critical cases in the final stage of the work when giving the final description of the manufacturing process.

We would like to stress the important positive features of methods of experimental design and data processing based on the statistical apparatus. First, this approach makes it possible to make a substantiated choice of bifurcation points because the scattering of the data in them is the greatest. Second, the significance of the coefficients of the regression equations gives a picture of the role of the variable factors in the process. Third, the ways of controlling the process and the optimum conditions for conducting it can be determined with minimum expenditures. There is no doubt that all the procedures envisage the creative participation of the experimenter. Experience shows that this plays a decisive role.

Let us give examples of controlling the process of fabricating a ceramic with a specified structure in order to provide the requisite level of properties [17 – 21]. The works had different aims, namely, the determination of the optimum conditions for manufacturing a dense ceramic with a specified chemical composition and the change in these conditions due to a change in the composition; the solution of a similar problem in the production of a dense ceramic from a binary powder mixture when the chemical reaction of synthesis of a new compound occurs in the roasting process and then the compound is sintered; the determination of the optimum conditions for a process aimed at attaining the specified parameters of a property or a set of properties. Methodologically, the main attention in both works was devoted to studying the behavior of model specimens in strictly controlled conditions. The subsequent technological experiments were conducted using methods of mathematical design.

Optimization was conducted with respect to the final parameter of the property, sometimes neglecting intermediate bifurcation points. It should be noted that the statistical methods automatically allowed for their effect, although the authors were not always interested in their physicochemical mechanisms. The results could have been better because the given set of experiments had the disadvantage of being carried out within one post-graduate, in a limited time, or with a limited number of experiments. Therefore, the accumulated statistical material was not very large although sufficient. For example, the interesting problems of the choice of the step in which the variable parameters should be varied and the effect of the step on variance of the reproducibility still remain unsolved. It would also be useful to understand where the optimum is for structures with cracks for the complicated case of using special refractories, when high strength should be combined with high thermal stability and low creep.

The model experiments on sintering were devoted to the behavior of specimens studied by accepted methods (the electrical conductivity was determined together with shrinkage or expansion of the specimens); the structure and properties of specimens hardened at various temperatures were investigated. The results were used for analyzing the mechanisms of the processes, establishing the bifurcation points and making recommendations on their elimination and reducing the noise level (internal fluctuations) in them. Then the processes were studied using methods of mathematical design of the multifactorial experiment (the case of "automatic" allowance for the bifurcations). In each stage, the structure and properties of the materials were studied too. This made it possible to establish the optimum parameters of the manufacturing process and realize them.

The main model tests were conducted for corundum pressings (in a study of sintering of single-phase powders) and for pressings with the composition of chrome-magnesium spinel (in a study of sintering of binary powder mixtures). The general laws obtained were proved experimentally for other kinds of ceramics as well (mullite, aluminomagnesia spinel, calcium, strontium and barium zirconates).

Direct experiments aimed at studying the shrinkage of single-phase powders together with their electrical conductivity and the strength, density, transfer numbers, specific surface area, and particle size showed that three processes follow each other in heating of oxide powder pressings, namely, cleaning and spheroidizing of the particle surface, partial sintering of the particles due to surface diffusion, and compaction by bulk diffusion. These processes are separated in time and temperature and are substantially nonuniform in space and time. In order to control effectively the behavior of the system at these bifurcation points, special recommendations were made for changing the heat treatment regimes.

In solid-phase interaction of the components of a binary mixture of powdered oxides, cleaning of the surfaces of the particles is followed by homogenization of the mixture in microvolumes due to heterodiffusion of the components which occurs together with partial sintering, and then the mixture is sintered fully. This was proved by the methods of dilatometric, x-ray diffraction, x-ray spectral, electron microscopic, and petrographic analysis.

In the first stage, we observed shifting of the reaction front and simultaneous formation of diffusion porosity. The formation of diffusion porosity causes an increase in the volume of the preform. The diffusion flows in microvolumes are substantially nonuniform due to the inhomogeneity of the chemical and granulometric compositions of the preforms, the porosity, the difference in the chemical activities of the particles, and the presence of a temperature gradient determined by the thermal conductivity of the regions and the reaction heat.

The set of these factors results in the formation of rather dense regions separated in the material by coarse pores and microcracks in the final stage of the interaction. The coarse pores appear due to coalescence of fine pores (internal sintering), cracks are formed due to the different changes in the volumes of some skeleton regions caused by local expansion (growth) or compaction. The growth kinetics depend on the individual properties of the components that affected the kinetics of the behavior of the system in heating. The curve of the variation of the linear sizes and their absolute values affect the phase transformations in the initial substances (the $\gamma - \alpha$ transformation in the aluminum oxide in synthesis of mullite), oxidation-reduction processes (the behavior of chromium oxide in the synthesis of chrome-magnesium spinel), hydration and carbonization (the effect of the pH of the medium in the synthesis of zirconates determined by the behavior of the alkaline-earth component). The total effect of all these processes determines the structure of the final product.

The growth kinetics change substantially if one of the components (in particular, chromium oxide in the synthesis of chrome-magnesium spinel) is represented by two fractions, i.e., finely and a coarsely disperse. At first the specimens expand due to the chemical reactions that occur in the finely milled part of the charge, followed by some shrinkage, and then secondary expansion which indicates involvement of the coarse fraction in the reaction.

Similar patterns of solid phase interaction were obtained in a study of the synthesis and sintering of other compounds. In the case of mullite, growth occurred due to predominantly one-sided diffusion of silicon; in the case of zirconates, it occurred due to diffusion of the alkaline-earth component. The observed differences were purely quantitative and involved the temperature of the beginning of the chemical interaction and its completion, the values of the expansion and shrinkage and their temperature ranges, and the properties of the materials obtained.

An increase in the volume of the preform was observed in all the studied systems, i.e., in mixtures with a composition corresponding to mullite, alumino- and chrome-magnesium spinels, and metazirconates of calcium, strontium and barium. The extent of the expansion and its temperature range depended on the structure of the pressing and the heating regime; the apparent activation energy of the process was structure-sensitive. The component of the reaction mixture that entered the cation part of the compound was more mobile and the component in the anion part was less mobile.

Thus, there are ways for effective control of the processes in this more complicated case (than single-phase ceramics). The solution consists in combining different techniques, namely, the directed change of the chemical, phase and granulometric compositions of the initial mixture and regimes of its heat treatment. The studies showed a principally new way of controlling the structure of ceramics with changes in their grain composition and the ratio of the components, which consists in the use of diffusion processes. This can give various materials, i.e., densely sintered, highly porous, and grained. The conditions for fabricating various kinds of ceramic materials with a composition corresponding to mullite, alumino- and chrome-magnesium spinels, metazirconates of calcium, strontium and barium were established. The special features of the processes of chemical interaction complicated by polymorphism, dehydration, decarbonization, and changes in the degree of oxidation of the components were described.

In conclusion, we would like to note that based on the general principles of the thermodynamics of nonequilibrium processes and synergetics, understood as the science of self-organization of natural processes, we can purposefully search for ways to improve the quality of ceramic materials. The specific ways in each case are determined by physicochemical processes that depend on the structure of the system and the conditions of its interaction with the environment. The probabilistic nature of the behavior of a system in a bifurcation requires the use of statistical methods for its description.

REFERENCES

1. H.-O. Pitegen and P. H. Richter, *The Beauty of Fractals. Images of Complex Dynamic Systems* [Russian translation], Mir, Moscow (1993).
2. V. S. Bakunov and A. V. Belyakov, "Prospects of improving the reproducibility of the structure and properties of ceramics," *Ogneup. Tekh. Keram.*, No. 2 (1997).
3. P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations*, Wiley, London (1971).
4. G. Nikolis and I. Prigozhin, *Self-Organization in Nonequilibrium Systems. From Dissipative Structures to Order through Fluctuations* [Russian translation], Mir, Moscow (1979).
5. H. Haken, *Synergetics*, Springer, Heidelberg (1978).
6. V. S. Bakunov and A. V. Belyakov, "On the problem of analyzing the structure of ceramics," *Neorg. Mater.*, **32**(2), 243 – 248 (1996).
7. V. S. Bakunov and A. V. Belyakov, "Thermal stability and the structure of ceramics," *Neorg. Mater.*, **33**(12), 1533 – 1536 (1997).
8. B. B. Mandelbrot, *The Fractal Geometry of Nature*, W. H. Freeman and Company, San Francisco (1982).
9. V. S. Ivanova, A. S. Balankin, I. Zh. Bunin, et al., *Synergetics and Fractals in Materials Science* [in Russian], Nauka, Moscow (1994).
10. E. Feder, *Fractals* [Russian translation], Mir, Moscow (1991).
11. T. A. Witten and L. M. Sander, "Diffusion-limited aggregation," *Phys. Rev.*, **27**, 5686 – 5697 (1983).
12. P. J. Meakin, "Diffusion-limited aggregation in three dimensions: results from a new cluster – cluster aggregation model," *Colloid. Interface Sci.*, **102**(2), 491 – 504 (1984).
13. E. A. Gudilin, N. N. Oleinikov, A. N. Baranov, and Yu. D. Tret'yakov, "Simulating evolution processes in polycrystalline systems that appear in crystallization of melts," *Neorg. Mater.*, **29**(11), 1443 – 1448 (1993).
14. Yu. D. Tret'yakov. N. N. Oleinikov, E. A. Gudilin, et al., "Self-organization of physicochemical systems in creating new materials," *Neorg. Mater.*, **30**(3), 291 – 305 (1994).
15. V. V. Kafarov, *Methods of Cybernetics in Chemistry and Chemical Technology* [in Russian], Khimiya, Moscow – Leningrad (1971).
16. S. L. Akhnazarova and V. V. Kafarov, *Optimization of Experiments in Chemistry and Chemical Technology* [in Russian], Vysshaya Shkola, Moscow (1978).
17. V. S. Bakunov, V. L. Balkevich, A. S. Vlasov, et al., *Ceramics from Highly Refractory Oxides* [in Russian], Metallurgiya, Moscow (1977).
18. S. S. Apoyan, T. V. Efimovskaya, V. S. Bakunov, and R. Ya. Popil'skii, "Some special features of solid phase synthesis and sintering of chrome-magnesium spinel in joint annealing," *Steklo Keram.*, No. 8, 32 – 34 (1977).
19. Kh. V. Kuliev, R. Ya. Popil'skii, and V. S. Bakunov, "Formation of the phase composition and sintering of magnesiochromite granular ceramics," *Steklo Keram.*, No. 6, 22 – 24 (1983).
20. A. V. Belyakov, R. Ya. Popil'skii, A. S. Vlasov, et al., "Synthesis of materials in the ZrO_2 – SrO system," *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, **24**(1), 80 – 83 (1988).
21. V. K. Vorob'ev, D. N. Poluboyarinov, and V. S. Bakunov, "Changes in conductivity in sintering of corundum ceramics," *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, **7**(5), 260 – 266 (1971).